Rapid Synthesis of Copper Zinc Tin Sulfide (CZTS) & Lead Perovskite Nanocrystals for Solar Cells & Associated Environmental Nanotoxicity

Kelly A. Collins

Abstract: Copper zinc tin sulfide (CZTS or Cu_2ZnSnS_4) and lead perovskite ($CH_3 NH_3 PbI_3$) nanoparticles were synthesized and then transformed to be dispersible in nonpolar solvents through an exchange reaction. These water soluble particles were then added to colonies of common *Shewanella oneidensis* bacterium and results of the effect of the particles on the bacterium are currently in process.

In completion of the Undergraduate Research Opportunities Program (UROP) at the University of Minnesota – Twin Cities

Under direction of Professor Eray Aydil of the Chemical Engineering & Materials Science Department

Motivation:

To synthesize copper zinc tin sulfide (CZTS or Cu_2ZnSnS_4) and lead perovskite ($CH_3 NH_3 PbI_3$) nanoparticles and observe their effect on the growth of the common bacteria strain *Shewanella oneidensis.*

Background:

Nanoparticles are an increasingly common component of many new technologies, yet the environmental impact they may harbor is still widely unexplored.

Biofilms are the most common arrangement of bacteria in the Earth's environment, thus studying the impact of nanocrystals on the growth and development of a common biofilm bacteria strain yields a generalizable representation of the nanoparticle toxicity. *Shewanella oneidensis* bacterium will be observed because these bacteria are found globally and represent a critical member of the ecosystem and food chain. In this experiment CZTS and lead perovskite nanoparticles will be synthesized and analyzed.

Procedure:

Synthesis of Lead Perovskite: 38.1 mg of lead (II) bromide and 6.4 mg of methyl ammonium bromide are each dissolved in 100 µL of DMF. Both solutions are gently heated and stirred to aid the dissolving process.

In a round flask 2 mL of ocadecene is combined with 95.8 µL of oleic acid and then 0.05 mmol tetraoctylammonium bromide. This solution is stirred and heated to 80º C, then both DMF solutions are added to the flask and the perovskite particles are immediately precipitated with acetone. This solution is then centrifuged at 4,000 rpm for 20 minutes, the supernatant is decanted, and the nanoparticles are dispersed in toluene.

Synthesis of CZTS: Three precursory solutions – $Cu(dedc)_2$, $Zn(dedc)_2$, and $Sn(dedc)_4$ – must be synthesized in order to produce the CZTS nanocrystals.

From the literature synthesis stated in L.C. Schmidt's "Nontemplate Synthesis of CH3NH3PbBr3 Perovskite Nanoparticles" article, $Cu(dedc)_2$ is produced by dissolving 9.0 g of sodium diethyldithiocarbamate trihydrate in 150 mL of reagent alcohol. In a separate reaction 4.23 g of copper(II) chloride is dissolved in 50 mL of reagent alcohol. The first solution is then slowly added to the second with constant stirring. A black precipitate will form which must be filtered and washed four times with deionized water to remove unwanted salts. To remove the water it must then be washed twice with acetone and dried in a desiccator under rough vacuum.

The procedure to produce $Zn(dedc)_2$ is identical for that of $Cu(dedc)_2$ except for the use of 3.38 g of zinc chloride in place of the copper(II) chloride.

$Sn(dedc)_4$ is produced by dissolving 9.6 g of sodium diethyldithiocarbamate trihydrate in 140 mL of reagent alcohol. In a separate reaction 3.0 g of tin(IV) chloride is dissolved in 50 mL of reagent alcohol. The first solution is added drop by drop to the second solution with constant stirring, as with the previous syntheses above. An orange precipitate will form. This precipitate must be rinsed thoroughly with deionized water and then two rinses with ice-cold acetone. This precipitate is then dried in a desiccator with a roughing pump for at least an hour. The crystal has thus formed, but it is necessary to purify it through recrystallization since possible side reactions like tin(II)-diethyldithiocarbamate may have formed. The orange powder is this time washed four times with deionized water, twice with cold acetone, and dried in a desiccator. The powder is then dissolved into 800 mL of boiling acetone while stirring vigorously. This solution boils until it becomes cloudy (at about 650 mL remaining) and the flask is then carefully removed from heat and allowed to cool to room temperature overnight. After this, the flask is the cooled

to -20 °C in a freezer for a total of one day. These newly formed crystals are then washed multiple times with ice-cold acetone and filtered to only keep the millimeter-sized reddish-orange crystals which are dried in a desiccator under rough vacuum. These crystals should be stored in a freezer.

Based on stoichiometry, 54 mg of $Cu(dedc)_2$, 27.2 mg of $Zn(dedc)_2$, and 53.4 mg of $Sn(dedc)_4$ yields about 30 mg of Cu_2ZnSnS_4 nanocrystals. These three powders are mixed with 4 mL of colorless or very faint yellow oleic acid and 1 mL of 1-octadecene. A yellow oleic acid indicated oxidation through air exposure during storage or distillation. This new mixture is heated to 60 °C while being stirred rapidly, then degassed at 10 mTorr for several minutes and purged with dry nitrogen gas in order to remove air from the flask. The degassing and purging are repeated three times. The resulting mixture is then heated to 140 °C under a continuous flow of dry nitrogen gas. All of the solids will be completely dissolved at this temperature within one minute. The solution should not, however, reach 175 °C in order to eliminate the chances of forming binary tin sulfide precipitates (*i.e.* SnS_2). This solution must then be cooled and kept at 75 °C.

In a separate reaction 10 mL of oleylamine must be similarly degassed and purged three times at 60 °C. This solution must then be heated to the desired synthesis temperature between 150-340 °C with constant stirring. This synthesis temperature will determine the average CZTS nanocrystal size produced.

The first mixture (stored at 75 °C) must then be extracted with a syringe and quickly injected into the flask containing the hot oleylamine. This reaction will turn black, bubble, and fume for several minutes. The addition of the first mixture causes the hot oleylamine temperature to drop by about 10-15%, but it quickly returns to its original oleylamine temperature in under

two minutes. After the reaction has passed this mixture must be stored under the fume hood for ten minutes. The flask must then be placed in a cold water bath to reduce it to room temperature. This is done in order to limit the handling of hot organics which can be very hazardous.

Lastly, the CZTS nanocrystals are precipitated by the addition of about 30 mL of reagent alcohol and centrifuging the solution for about 5 minutes. The supernatant is then discarded and the nanocrystals are dispersed in about 1 mL toluene by sonication after adding about 0.3 mL of neat oleic acid. The crystals are then washed with the 20 mL of the reagent alcohol and centrifuged for five minutes again. The final step in producing the desired CZTS nanocrystals is to discard the colorless supernatant and re-disperse the nanocrystals in 1 mL toluene with 0.01 vol% oleic acid and sonicate it for an hour.

Exchange Reaction: The exchange reaction is performed identically for both the perovskite and CZTS nanoparticles. First, 0.55 g of potassium sulfate or citric acid (depending on the trial) is dissolved in 1 mL of deionized water and 2 mL of formamide. This process is accelerated by sonicating and gently heating the vial. 1 mL of 2 mg/mL solution of particles (either perovskite or CZTS) dispersed in toluene is then added to the vial and stirred for about three hours (the reaction should be stirred for more than one, but less than sixteen hours).

Once the stirring has been stopped 1 mL of toluene is added to each vial and allowed to sit for five minutes to separate. The toluene layer is then removed from the top of the vial with a pipette and 2 mL of acetonitrile is added to precipitate the particles from the formamide containing potassium sulfate or citric acid. This solution is centrifuged at 4,000 rpm for 20 minutes and the supernatant is then decanted.

To clean the nanoparticles they are re-dispersed in 2 mL of fresh formamide and sonicated for about one minute. Then 2 mL each of acetonitrile, acetone, and toluene are added

to precipitate the particles. This solution is then centrifuged at 4,000 rpm for 20 minutes and the supernatant is decanted. This cleaning process is repeated three times and after the final supernatant is decanted the particles are re-dispersed in deionized water and sonicated for about one minute.

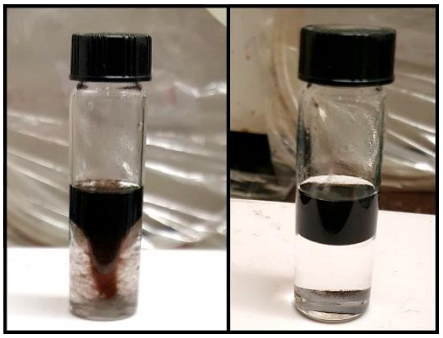

Figure 1 - During (left) and after (right) the exchange reaction of CZTS nanoparticles. Note the mix of stirring layers separates into (from top to bottom) a thin layer of toluene,a thick layer of particles, and discardable supernatant.

Discussion:

The samples were made following the literature procedure and yielded concentration of 6 mg/mL. The synthesis of lead perovskite particles is a more recent chemical discovery, thus synthesis was carried out, but the particles are still in a state of being tested with x-ray diffraction and transition electron microscopy to determine characteristics and stability before nanotoxicity trials are conducted. For these reasons the exchange reaction and nanotoxicity studies have only been minimally performed with the CZTS particles at this time.

The particles were soluble in nonpolar solvents when initially synthesized, but, in order to test their effects on bacteria, they needed to be dispersible in water as to not harm the bacteria samples with a nonpolar solvent. The exchange reaction previously described was carried out for CZTS particles and the separation was apparent and as expected, as shown in Figure 1. The particles were then cleaned in the process previously described and dispersed in water for testing with the bacteria.

The water dispersed CZTS particles were then given to our collaborator Christy Haynes in the chemistry department of the University of Minnesota for exploration of their reaction with bacteria, which is currently in progress.

Future Goals:

Once the lead perovskite particles have been characterized they will also undergo the exchange reaction to become dispersible in water. Both particles can then be examined at various concentrations with bacteria to determine what effects they may have on the environment.

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